ON THE PROPERTIES OF NITROGEN IN NITROGENOUS CARBONS AS COMPARED WITH THE PROPERTIES OF NITROGEN IN COKE. [1])

BY

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§ 1. *Introduction.*

When bituminous coal is carbonized, about 50—70 % of the nitrogen of the coal is found in the coke. This nitrogen is firmly bound as it is only at temperatures from about 800° upwards that it is gradually split off in the form of elementary nitrogen. Several authors have suggested that the nitrogen in coke is combined chemically to the carbon.

As early as 1889 L. Mond [2]) showed that by heating coke in a current of superheated steam, ammonia is formed abundantly. Sachs [3]) showed that 89 % of the nitrogen of coke could be transformed into ammonia by the action of superheated steam under suitable conditions, and Cobb [4]) obtained a conversion of even 95 %. Pexton and Cobb [5]) showed that during the gasification of coke by means of superheated steam the ratio C : N remained fairly constant in the residual coke during the greater part of the reaction, while Salmang [6]) obtained similar results. All these observations are in accordance with the supposition that the nitrogen in coke is chemically bound to carbon in such a manner, that the combined nitrogen has the same properties as in a nitrile group.

However, none of the former investigators have studied the coke obtained from ash-free coal. We have prepared coke from samples of bituminous coal, which were previously freed from mineral substances; these coke samples contained about 0,3 ash and 1,7—1,8 %

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[1]) Dissertation of P. H. van der Ley, Amsterdam 1929. A short account of the results of this investigation has been communicated in a paper "On the forms of sulfur and nitrogen in coke and on the fixation of sulfur and nitrogen by amorphous carbon at high temperatures", read by Wibaut at the „Third International Conference on Bituminous Coal" held at Pittsburgh in November 1931, which paper has been published in the proceedings of this conference.

[2]) J. Soc. Chem. Ind. 1899, 505.

[3]) Dissertation Karlsruhe 1913.

[4]) W. Young Memorial Lecture 1918.

[5]) Gas J. **163**, 160 (1923); Gas World **78**, 619 (1923).

[6]) Z. angew. Chem. **32**, 148 (1919).

nitrogen, which must be present in a chemical combination with carbon. With the purpose of obtaining more insight into the kind of chemical combination of the nitrogen in coke, we have synthesized nitrogenous carbons in different ways and compared the properties of the nitrogen in these products with the properties of the nitrogen in coke.

It is well-known that amorphous carbon does not take up any nitrogen when it is heated in a current of pure nitrogen even at high temperatures. If more or less pure amorphous carbon is heated in gaseous ammonia, hydrocyanic acid is formed, but the remaining carbon contains nitrogen which has been fixed during the reaction, as has been shown by Mixter. [7]) This investigator heated "lampblack" in a current of gaseous ammonia at "red heat" and obtained a nitrogenous carbon which contained 3 % nitrogen; when cyanogen was used instead of ammonia the nitrogen content of the resulting product was 6,5 %.

We have made similar experiments as Mixter but under well defined conditions of gas-flow and temperature and using samples of pure amorphous carbon of different origin, as well as the crystalline carbon modifications, diamond and graphite. While these crystalline substances do not fix any nitrogen, we obtained nitrogenous carbons from amorphous carbon as a starting material.

Of the known organic nitrogen compounds which contain no other elements than carbon and nitrogen, there are two substances which are amorphous solids and show more or less the appearance of amorphous carbon. The one is paracyanogen and the other is a substance of the composition $(C_3N_2)x$ which was obtained by Pauly and Waltzinger [8]) by the thermal decomposition of tetraiodoglyoxaline.

Another substance of the appearance of amorphous carbon which contains hydrogen besides nitrogen, has been prepared by Pauly and Waltzinger by the thermal decomposition of tetraiodopyrrole. We have prepared these substances and compared their properties with those of nitrogenous carbons derived from amorphous carbon and with the coke samples referred to.

We will first give a description of the experiments and afterwards a discussion of the results.

EXPERIMENTAL PART.

§ 2. *Analytical method.*

The determination of the nitrogen content of our samples of coal and coke and of our nitrogenous carbons has been carried out by the method given by Ter Meulen [9]) for the analysis of coal and coke. This excellent method gives reliable results for this class of

[7]) Am. J. Sci. (3), **45**, 373 (1893).
[8]) Ber. **46**, 3134 (1913).
[9]) Rec. trav. chim. **43**, 643 (1924); ibid. **46**, 284 (1927).

substances, while the figures obtained by the Kjeldahl method are often too low, as has been shown by Terres [10]) and by Ter Meulen. The micro-Dumas method of Pregl is not convenient in this case, as it is difficult to obtain a complete combustion of these nitrogenous carbons. In applying the method of Ter Meulen to graphite it was found necessary to heat several times with a fresh quantity of sodium carbonate in order to obtain complete decomposition. Diamond powder could be gasified in one operation by this method.

§ 3. *Preparation of coke from nearly ash-free coal.*

Samples of bituminous coal (gas-coal from the Ruhr district) were finely powdered (sieve 900 meshes per square cm) and extracted with boiling hydrochloric acid of 25 %, with hot hydrofluoric acid and again with hot hydrochloric acid, followed by thoroughly washing with boiling water, till the ash content remained about 0,2 %. The extracted coals contained no halogen. A platinum crucible, containing 2,8 g of the coal sample was put in an electrical furnace, which had been heated previously to 1000°; the crucible was heated for 20 or 30 minutes at this temperature. The results are given in table I.

TABLE I.

	Ash	Nitrogen
Coal sample 1.		
Coal before extraction	2,4 %	1,72 %
Coal after extraction	0,2 %	1,69 %
Coke from extracted coal		
a. Time of coking 20 minutes, yield of coke 68,5 %	0,3 %	1,8 %
b. Time of coking 30 minutes	—	1,7 %
Coal sample 2.		
Coal before extraction	2,4 %	1,72 %
Coal after extraction	0,2 %	1,7 %
Coke from original coal		
(Time of coking 20 minutes, yield of coke 68 %)	3,5 %	1,7 %
Coke from extracted coal		
a. 20 min. coking, yield 68 %	0,3 %	1,7 %
b. 30 min. coking, yield 66 %	—	1,65 %

These experiments show that the nitrogen content of the coal is not diminished by the extraction with acids and that the nitrogen content of the coke is independent of the ash content. The nitrogen in the coke must therefore be present in organic combination.

§ 4. *Preparation of nitrogenous carbons by the action of ammonia or of cyanogen on amorphous carbon.*

The following samples of carbon were used for these experiments.

1°. **Amorphous carbon (sample 1).**

Pure sucrose was charred in a nickel crucible and the charcoal obtained was finely powdered and sieved (900 meshes to a square cm); this charcoal was heated in a porcelain tube at about 600° and 20 mm. When most of the volatile substances had been expelled, we heated the porcelain tube for 18 hours at 1000° while a

[10]) J. Gasbeleucht. 62, 173 (1919).

vacuum of 1—0,4 mm was maintained; from 41 g. charcoal, 27 g. outgassed amorphous carbon were obtained; ash content 0,17 %.

2°. **Activated carbon (sample 2)** was prepared by heating small lumps (size of a pea) of sugar carbon in a quartz crucible at 950°, with limited air supply, according to the method of Bartell and Miller [11]); the product was powdered as sub. 1°.

3°. **Norit (sample 3).**

A commercial sample of "Supra Norit" was outgassed in the same way as described sub 1°. The product consisted of a fine powder, ash content 0,31 % (unsoluble in hydrochloric acid), nitrogen content 0.25 %.

4°. **Diamond powder and purified Ceylon graphite.**

These samples were the same that have been described by Wibaut and van der Kam [12]) (ash content of the diamond powder 0,067 %, of the graphite 0,027 %).

Description of apparatus and experimental method used for the heating of carbon samples in ammonia and cyanogen.

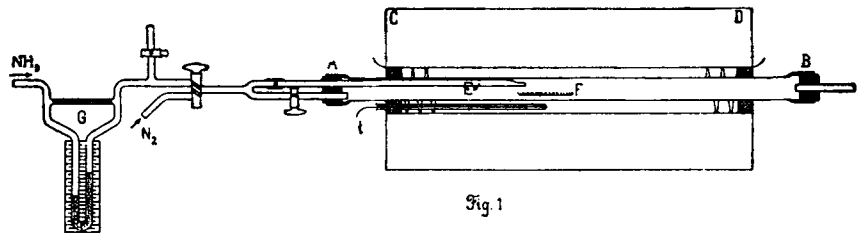

Fig. 1

The reaction tube of porcelain AB (length 57 cm, internal diameter 24 mm) was heated in an electrical furnace CD, which was so designed that a constant temperature (oscillations about 3°) was obtained in the reaction tube over a length of 25 cm. The temperature is measured with a thermo-couple t which is fitted at the outside of the reaction tube and which is connected with a millivoltmeter.

Experiments with ammonia.

The ammonia gas taken from a steel bomb containing the commercial product, passes a drying tube filled with calcium oxide and a flow meter G filled with paraffin oil and enters the reaction tube through a quartz tube E. The outlet of this tube is just above the porcelain boat F which contains 0,75 grams of amorphous carbon. Before the beginning of an experiment the reaction tube was exhausted to about 1 mm and then heated to the desired temperature; a current of ammonia gas is then passed through the tube during a definite time; the outlet gases of the tube are passed through a solution of potassium hydroxide, to absorb the hydrocyanic acid formed in the experiment.

When the experiment is finished, a current of pure dry nitrogen is passed through the reaction tube for two hours at 500° to expel the ammonia and the tube is allowed to cool in a stream of nitrogen; the remaining carbon is weighed and its nitrogen content is determined.

In table II the results obtained with amorphous carbon (sample I) are given:

[11]) J. Am. Chem. Soc. **44**, 1866 (1922).
[12]) Rec. trav. chim. **41**, 120 (1930).

TABLE II.

Rate of flow of NH_3 gas 10 litres per hour.

Time of heating in hours	Temperature	Nitrogen content of resulting carbon	% of carbon converted into HCN.
3	500°	0,2	—
3	600°	0,4	—
3	700°	1,2	0,8
24	700°	1,3	—
3	800°	0,8	15,4
3	900°	0,9	45,7

The figures show that under these conditions the maximum content of fixed nitrogen in the carbon is obtained at a reaction temperature of 700° and that a state of equilibrium is nearly established in 3 hours. The reaction between gaseous ammonia and amorphous carbon is reversible for when the nitrogenous carbons obtained, are heated in a current of hydrogen, ammonia is formed. This is the reason why the rate of flow of ammonia must be relatively high to obtain fixation of nitrogen by the carbon, for otherwise a great part of the ammonia is decomposed at these high temperatures and the flowing gases contain much hydrogen, so that the conditions for nitrogen fixation by the carbon are unfavourable. For example we obtained a nitrogenous carbon containing 0,25 % N in an experiment, wherein the carbon was heated for 12 hours at 800° and the rate of flow of ammonia was 1 l per hour.

The figures given in table II are reproducible if the conditions of the experiment are the same. If the distance between the boat containing the carbon and the outlet of the tube E is increased much less nitrogen is fixed by the carbon. Obviously the reason is that under these conditions a great part of the ammonia is decomposed before it can react with the carbon. If these nitrogenous carbons are heated in a current of dry nitrogen up to 950°, a considerable part of the fixed nitrogen is split off, but no ammonia could be detected in the issuing gases. When the nitrogenous carbons are heated with diluted hydrochloric acid at 100°, no ammonium chloride is formed. It follows from these experiments that the nitrogen content of these products is not due to ammonia in a form of absorbtion.

In table III the results of experiments with other kinds of carbon are given:

TABLE III.

Rate of flow of NH_3 gas 10 litres per hour.

Sample of Carbon	Duration of experiment	Temperature	Nitrogen content of resulting carbon.
Norit	½ hour	700°	1,3 %
„	3 hours	700°	2,6 %
„	24 „	700°	2,9 %
„	3 „	800°	3,1 %
„	3 „	900°	2,9 %
Activated carbon	3 „	700°	2,5 %
Diamond powder	3 „	700°	0 %
Powdered graphite	3 „	700°	0 %

It follows from these experiments that the amount of nitrogen that is fixed by the amorphous carbon, depends on the properties of the carbon sample used. Activated carbon and norit fix much more nitrogen than non activated carbon under the same experimental conditions. The crystalline modifications of carbon, diamond and graphite do not fix a trace of nitrogen.

Experiments with cyanogen.

Pure cyanogen [13]) was obtained by heating mercuric cyanide at 400°—500°, drying the gas over phosphorus pentoxide and condensing it at –80° in a glass tube; the glass tube was sealed and kept until use. For carrying out an experiment the tube with liquid cyanogen was immersed in a refrigerating mixture at about –18° (at this temperature the vapour pressure of liquid cyanogen is somewhat above 760 mm) and the tube was connected by means of a stop cock with the reaction tube which contained the sample of carbon. The rate of flow of the cyanogen gas was regulated at 2 liters per hour; the duration of each experiment was 3 hours. After the experiment the cyanogen was expelled from the reaction tube by a current of nitrogen for 1½ hours and the tube was allowed to cool down in a slow stream of nitrogen. In table IV some results are given.

TABLE IV.

Temperature	% of nitrogen fixed by		
	Non-activated carbon	Activated carbon	Norit
700°	2,2	—	10,3
800°	1,5	7,5	10,6
900°	0,8	—	8,6

The nitrogen content of the nitrogenous carbons obtained by the action of cyanogen on carbon is therefore considerably higher than in the experiments with ammonia. Here again we see that the products obtained from activated carbon and norit have a much higher nitrogen content than those obtained from non-activated carbon. It is probable that part of the nitrogen in these carbons is present in the form of absorbed paracyanogen as will be pointed out afterwards.

The X ray investigation of a substance containing 10 % nitrogen was carried out by Dr. J. R. Katz; the Röntgenograms obtained were identical with those of the untreated norit.

§ 5. *Preparation of paracyanogen and of the nitrogenous carbons of Pauly and Waltzinger.*

Paracyanogen was obtained as a byproduct during the preparation of cyanogen from mercuric cyanide. The crude paracyanogen was heated for several hours at 500° in a current of nitrogen, in order to free it from small quantities of mercury. The nitrogen content of our product was 53,7 %, calculated for $(CN)_x$ 53,8 %. We have also tried to prepare paracyanogen by the method of Klason, i.e. thermal decomposition of cyanuric iodide, obtained by action of hydrogen iodide on cyanuric chloride. We did not succeed in obtaining

[13]) Compare Terwen, Z. physik. Chem. **91**, 469 (1916).

pure paracyanogen by this method; our product, which showed a red brown colour, contained 50,2 % N.

Preparation of $(C_3N_2)x$.

Glyoxaline was prepared by the method of Fargher and Pyman.[14]) The splitting off of carbon dioxide from the glyoxaline dicarbonic acid was done by heating the pure dry acid in quantities of 3 gram in a retort; the glyoxaline was crystallized from benzene, melting point 88°; yield 3—4 g from 15 g dicarbonic acid. For the preparation of tetraiodoglyoxaline the prescription of Pauly and Waltzinger[8]) was followed; we obtained 41 g from 6.8 g glyoxaline (iodine found 88,1 % and 88,7 % calculated 88,6 %).

The tetraiodoglyoxaline was heated at 200° in an evacuated glass tube during several hours; the reaction product was powdered and extracted with boiling carbon tetrachloride to remove iodine; the resulting amorphous mass was then again heated during one hour at 420°—430° in an evacuated glass tube. From 6,4 g of tetraiodoglyoxaline we obtained 0,7 g of a soft velvety black powder, which contained 40,5 % N and only a trace of iodine. (calculated for C_3N_2 43.7 % N). Pauly and Waltzinger have carried out the heating of the tetraiodoglyoxaline in a current of carbon dioxide; the analysis of their product was in good accordance with the theoretical values. Our product was evidently decomposed to a slight degree, but this circumstance is of no importance for our purpose.

Decomposition product of tetraiodopyrrole.

The following method for preparing tetraiodopyrrole was satisfactory[15]): 10 g pyrrole were stirred with a solution of 24 g sodium hydroxide in 500 g water; a solution of 150 g iodine and 100 g potassium iodide in 1 L water was slowly added. The liquid obtains a dark green colour; the iodine compound separates in the form of a yellow solid; the reaction is finished when the liquid has obtained a brown colour. The solid is dissolved in alcohol, the solution boiled with decolorizing charcoal and the tetraiodopyrrole is precipitated from the alcoholic solution by water as yellow white crystals, yield 65 g or 77 % of the theoretical (iodine found 88,6 % and 88,3 %, calculated 88,96 %).

Pauly and Waltzinger[8]) studied the thermal decomposition of this compound; they give no details of the reaction, but state that the final product, a substance of the external appearance of amorphous carbon, contained 19,7 % N (calculated for $(C_4NH)x$ 22,2 % N).

Ciusa[16]) has also studied the thermal decomposition of tetraiodopyrrolle; he calls the resulting product "pyrrole graphite" and ascribes to it the formula $(C_4NH)x$, but no analysis of this final product is given in his paper.

According to our experience the preparation of a substance of the empirical composition C_4HN from tetraiodopyrrole is difficult to realise.

The best results were obtained as follows: tetraiodopyrrole is heated in a current of pure nitrogen; the decomposition begins at about 140°, while iodine vapour is formed vigorously; after heating two hours at 155°—165°, a reaction product is obtained which contains 65,2 % J and 7,7 % N. (Calculated for (C_4HNJ) 66,8 % J and 7,4 % N). These results are in accordance with the statement of Ciusa. The reaction product, an amorphous black substance, was finely powdered and heated for one hour at 450° in a current of nitrogen; it is not possible to obtain a product free from iodine by heating at 200°; if the

14) J. Chem. Soc. **115**, 227 (1929).

15) Compare D. R. P. 38423, Friedländer; Fortschritte der Teerfarbenfabrikation I, 223.

product is heated higher than 450°, nitrogen is split off in the form of ammonia or ammonium iodide. This difficulty does not occur in the thermal decomposition of tetraiodoglyoxaline, as this substance contains no hydrogen. Our final product, a black amorphous powder, contained 19,4 % N and only a trace of iodine. This is in accordance with the statement of Pauly.

Experiments to prepare nitrogenous carbons by the action of nickel carbonyl at room temperature on an ethereal solution of cyanuric chloride or tetraiodopyrrole gave negative results; no reaction occurred.

The X-ray investigation of the nitrogenous carbons from tetraiodoglyoxaline and from tetraiodopyrrole has been carried out by Dr. J. R. Katz, to whom we express our thanks. The Röntgenograms of these substances did not show interference lines of graphite and showed the type for amorphous substances. There seems to be no reason to call the product obtained from tetraiodopyrrole "pyrrole graphite" as has been done by Ciusa.

§ 6. *Thermal decomposition of the nitrogenous carbons by heating in a current of nitrogen or in a vacuum.*

A porcelain boat containing 0,2—0,6 g of nitrogenous carbon was placed in a quartz tube, which was heated in an electrical furnace, while a slow stream of dry pure nitrogen was passed through the tube. The issuing gases were washed with potassium hydroxide and the amount of potassium cyanide was determined after the experiment, by precipitating with silver nitrate, solving the silver cyanate with nitric acid and weighing the silver cyanide on a Gooch crucible. The amount of cyanogen formed during the decomposition of the nitrogenous carbon was calculated according to the equation:

$$(CN)_2 + 2\ KOH = KCN + KCNO.$$

The following results were obtained: 0,1985 g $(C_3N_2)x$ (containing 0,0804 g nitrogen) heated for 5 hours at 860°—880°; 0,078 g nitrogen was split off in the form of $(CN)_2$; weight of residue 0,0468 g, containing 6,6 % N.

This result is in accordance with Pauly who states that this nitrogenous carbon is decomposed at 800°—900° almost quantitatively according to the equation $(C_3N_2)x = Cx + x(CN)_2$ but that the resulting „Carbon" contained still about 10 % nitrogen.

0,078 g **paracyanogen** (containing 0,042 g nitrogen) heated for one hour at 900°; 0,405 g nitrogen was split off in the form of $(CN)_2$; weight of residue 0,004 g. The paracyanogen is therefore quantitatively decomposed into cyanogen at this temperature.

Nitrogenous carbon from tetraiodopyrrole. The thermal decomposition of this substance occurs more slowly. 0,2 g substance (containing 0,039 g nitrogen) were heated during seven hours at 900°; 0,0297 g nitrogen was split off in the form of $(CN)_2$; the residue weighed 0,136 g and contained 4,8 % N. This substance was heated again for 5 hours at 900°, only a trace of cyanogen was formed in this experiment; the resulting nitrogenous carbon contained 0,006 g nitrogen. Under these conditions 75 % of the nitrogen is split off in the form of cyanogen while a smaller part remains in the nitrogenous carbon.

Nitrogenous carbon prepared from norit and cyanogen at 900°.

0,263 g (containing 0,0226 g nitrogen) heated for 4 hours at 930°—950°; 18,7 % of the nitrogen was split off in the form of $(CN)_2$, 44,6 % was split off as elementary nitrogen, while 36,7 % of the nitrogen was present in the residue, which weighed 0,247 g and showed a nitrogen content of 3,1 %.

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[16]) Gazz. chim. ital. **52**, II, 130 (1922); **55**, II, 384 (1925).

Nitrogenous carbon prepared from non-activated carbon and ammonia at 700°, N content 1,2 %.

0,620 g were heated for 5 hours at 950°; the nitrogen content of the residue was 0,55 %, but no trace of cyanogen had been formed. The nitrogen is split off in elementary form.

The same holds for the **coke from ash-free coal.** Here again the nitrogen is slowly split off at 950°, but no cyanogen is formed.

The heating of the nitrogenous carbons in vacuum was carried out in a quartz tube which was connected with a mercury manometer; the apparatus was evacuated with an oil pump.

Under these circumstances paracyanogen is already decomposed for 60 % at 750°. The decomposition of the substance $(C_3N_2)_x$ begins already at 525°; 16 % of the nitrogen is split off after two hours heating at this temperature. The temperature was then raised in four hours to 860° and kept at this point for two hours. It was found that 92 % of the nitrogen had been split off, while the resulting carbon contained about 10 % of nitrogen.

The decomposition of coke from ash free coal occurs much more slowly under these circumstances. The evolution of nitrogen begins at about 800°, after heating for 10 hours at about 1000°; while the apparatus was continually evacuated, the nitrogen content of the coke had decreased from 1,8 % to 0,4 %.

These experiments therefore show that the thermal decomposition of paracyanogen and of the nitrogenous carbons prepared from tetraiodoglyoxaline or from tetraiodopyrrole occurs at much lower temperatures than the thermal decomposition of the nitrogen-carbon-complex which is present in coke. Another point of difference is that during the thermal decomposition of the first three substances, the greater part of the nitrogen is split off in the form of cyanogen, while no trace of cyanogen is found during the decomposition of coke.

The nitrogenous carbons prepared from ammonia and amorphous carbon show the same behaviour as coke, when submitted to thermal decomposition.

§ 7. *Action of hydrogen on nitrogenous carbons.*

A porcelain boat containing a weighed quantity of nitrogenous carbon (0,02—0,2 grams depending on the nitrogen content of the preparation) was placed in a quartz tube (internal diameter 1 cm) which could be heated up quickly to the desired temperature by means of an electrical furnace. A current of pure dry hydrogen was passed through the quartz tube at a constant rate of 1,4 litres per hour (0°, 760 mm); the rate of gas-flow was the same in all the experiments. The gases issuing from the reaction tube passed through a second quartz tube which was filled with nickel asbestos and which was heated in a suitable furnace at 350°. The purpose of the nickel asbestos was to convert any cyanogen formed into ammonia. This tube was only used with these nitrogenous carbons from which cyanogen is split off during the thermal decomposition, as had been found by the experiments already described.

The gaseous mixture issuing from the apparatus passed through a beaker, containing 0,01 n. hydrochloric acid and methyl orange. The amount of ammonia formed was determined at definite time intervals by

adding 0,01 n. hydrochloric acid from a burette. In this manner the amount of ammonia which was formed by the action of hydrogen on the nitrogenous carbon under the conditions of the experiment and at a constant temperature, was determined as a function of the time.

It was found that the rate at which nitrogen is split off in the form of ammonia at a constant temperature, decreased with the time; when the rate of the reaction had become very slow, the temperature was quickly raised and again kept constant at a desired value. The formation of ammonia starts again, to decrease again after a certain time. In fig. 2—5 the results of these experiments are represented. The quantities of ammonia formed are calculated in percentages of the original nitrogen content of the nitrogenous carbon. [17])

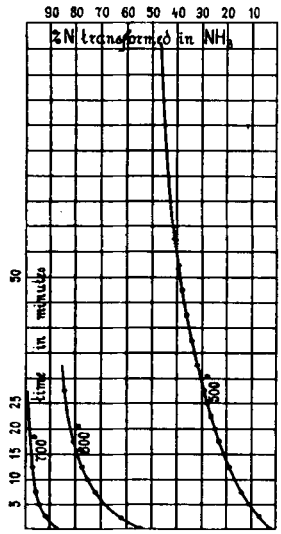

Fig 2

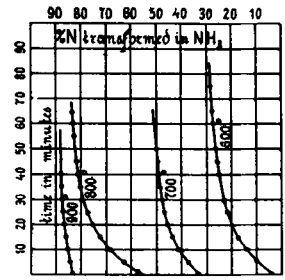

Fig 3

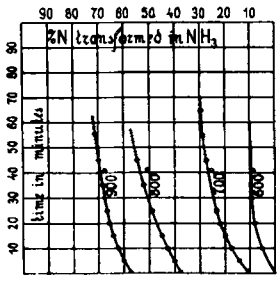

Fig 4

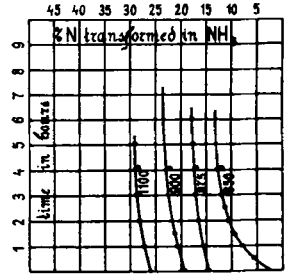

Fig 5

[17]) The numerical values are given in the dissertation of van der Ley.

It must be noticed that at the higher temperatures an unknown part of the ammonia will be decomposed in the reaction tube; only the amount of ammonia actually present in the outlet gases has been determined. Fig. 2 refers to a nitrogenous carbon obtained from tetraiodoglyoxaline, which contained 40,5 % nitrogen. Fig. 3 refers to a nitrogenous carbon obtained by heating norit in a current of cyanogen at 700° and which contained 10,3 % nitrogen. Fig. 4 refers to a nitrogenous carbon obtained by heating amorphous carbon in a current of ammonia at 750° and which was afterwards heated in a current of nitrogen at the same temperature. The nitrogen content of this nitrogenous carbon was 0,75 %. Fig. 5 refers to coke obtained from ash-free coal; the nitrogen content of this sample was 1,8 %.

It will be seen from these curves that there is a great difference in reactivity towards hydrogen for the different kinds of nitrogenous carbons. The decomposition of the nitrogenous carbon prepared from tetraiodoglyoxaline is already important at 500°, while the nitrogen carbon prepared from amorphous carbon and ammonia still retains most of its fixed nitrogen after being heated at 700°.

In the case of coke prepared from ash-free coal the formation of ammonia is scarcely sensible at 750° and is slow even at 1100°, the time unit for the curves of coke has been taken in hours, while in the other cases the time unit was in minutes.

§ 8. *Discussion of the results.*

It follows from our experiments that the nitrogen in coke is bound with chemical valency forces to carbon and that this "carbon-nitrogen complex" in coke is much more stable at high temperatures than paracyanogen or than the substance $(C_3N_2)x$, or the nitrogenous carbon derived from tetraiodopyrrole. These substances may be considered as polymeric compounds of an approximately definite composition; in the second and the third the nitrogen is present in the form of a condensed heterocyclic ring system.

While the thermal decomposition of these compounds begins already at about 500° and is nearly complete at 800°—900°, whereby 80—90 % of the nitrogen is split off in the form of cyanogen, the thermal decomposition of the carbon-nitrogen-complex in coke begins only at about 800° and the reaction is still slow at 1000°; the nitrogen is split off in elementary form, no cyanogen being observed.

However the residue of the thermal decomposition of these polymeric compounds derived from glyoxaline or from pyrrole is a nitrogenous carbon containing 4—6 % nitrogen, which is not split off or only very slowly at 900°. The condensed nitrogenous heterocyclic rings are obviously for the greatest part destroyed by heating, but in the resulting product there remains a part of the nitrogen combined to carbon in a form, which is stable at high temperatures.

It is well known that in the combustion analysis of nitrogen compounds often nitrogenous carbons are obtained, which are very resistent towards combustion.

In the behaviour towards hydrogen of the nitrogen-complex in coke and the nitrogenous carbons mentioned, similar differences have been found as in the thermal decomposition. Here again the nitrogen in

coke is much less reactive than the nitrogen in the products derived from pyrrole or from glyoxaline.

The nitrogenous carbons which show the greatest analogy with the carbon-nitrogen-complex of coke, are the substances obtained from amorphous carbon and ammonia. In these substances the nitrogen is certainly not present in the form of adsorbed ammonia, as follows from our experiments. The nitrogen cannot be present in the form of adsorbed nitrogen molecules — which are formed by the decomposition of ammonia at the temperatures at which these products are prepared —, as the nitrogen in these nitrogenous carbons is transformed into ammonia by the action of hydrogen at ordinary pressure from temperatures of 600° upwards.

The nitrogen must therefore be chemically bound by the carbon atoms. From the fact that these nitrogenous carbons cannot be prepared from the crystalline modifications of carbon, we conclude that the nitrogen atoms in these products are fixed to the unsaturated surface atoms of the amorphous carbons. It seems probable that a surface carbon atom which has three free valencies reacts with ammonia, whereby hydrogen is split off and the nitrogen atom of the ammonia molecule is fixed by the carbon atom, so that a nitrile group is formed. These nitrogenous carbons should therefore be considered as *surface compounds, in which nitrile-groups are present at the surface.* The fact that norit and activated carbon yield nitrogenous carbons of a higher nitrogen content than non-activated amorphous carbon is in accordance with this supposition.

There are many analogies between these nitrogenous carbons, prepared from amorphous carbon and ammonia and the sulphurous carbons of low sulphur content, which have been studied in this laboratory. [18]) In these products nitrogen or sulphur are chemically bound to carbon, while the substances do not show a stoechiometrical relation between carbon and sulphur.

It is probable that in the nitrogenous carbons obtained by the action of cyanogen on amorphous carbon, a part of the nitrogen is present in the form of -CN groups, which are fixed by the unsaturated surface atoms of the amorphous carbon; here again there would be formed a surface compound, which contains nitrile groups at the surface. From the fact that during the thermal decomposition of these substances a considerable amount of cyanogen is formed, while no trace of cyanogen is split off by decomposition of the nitrogenous carbons prepared by the action of ammonia, it seems probable that in the nitrogenous carbons obtained by the action of cyanogen, a part of the nitrogen is present in the form of adsorbed paracyanogen. Another part of the nitrogen in these substances is however very firmly bound to the carbon as a nitrogenous carbon, containing 3 % nitrogen remained after the heating of these cyanogen carbons at 950°.

Returning now to the nitrogen-carbon-complex in coke, it can be

[18]) Rec. trav. chim. **41**, 153 (1922); **43**, 731 (1924); **49**, 121 (1930).

said that the nitrogen in coke shows the same properties as the nitrogen in a nitrile group, which follows from the fact that the nitrogen is split off in the form of ammonia, either by the action of steam or of hydrogen at high temperatures.

The nitrogen in coke is certainly not present in the form of paracyanogen or of the condensed heterocyclic ring-systems which are treated in this paper. It would be possible of course that other more stable heterocyclic ring-systems containing nitrogen atoms are present in coke, but as far as our experiments go, the nitrogenous carbons, which show much analogy to the carbon-nitrogen-complex in coke, are the products obtained from amorphous carbon and ammonia, and to a certain extent also the nitrogenous carbons obtained from amorphous carbon and cyanogen.

Terres [19]) studied the thermal decomposition of various organic compounds containing nitrogen and found that only compounds containing the amide group and the imide group, present in open or closed chains, are able to split off nitrogen in the form of ammonia. From this fact and from extraction experiments with coals he concludes that the nitrogenous substances in coals are of proteïn origin. If this is true, the carbon-nitrogen-complex of coke would be formed by the thermal decomposition of compounds in which the nitrogen is present in the form of amido or imido-groups. This would be to a certain point analogous to the formation of nitrogenous carbons from ammonia and amorphous carbon.

However this may be, we have shown that nitrogenous carbons which contain the nitrogen in the form of a stable carbon-nitrogen-complex presumably as a surface compound can be prepared and that these substances represent a possible model for the nitrogen-carbon-complex in coke, which is so remarkably stable at high temperatures. The fact that only those nitrogenous carbons, which contain a low nitrogen content (a few percents) are stable at high temperatures, is in accordance with the supposition that in all these products, which may be prepared either starting from amorphous carbon or by thermal decomposition of $(C_3N_2)x$ or of $(C_4HN)x$ the remaining nitrogen is present in the form of a surface compound.

Summary of results.

1°. Nitrogenous carbons have been prepared by the action of ammonia or of cyanogen on amorphous carbon at temperatures from 500°—900°; neither diamond powder nor graphite reacts with ammonia under these conditions.

2°. The thermal decomposition and the decomposition by hydrogen at elevated temperatures of these nitrogenous carbons has been studied

[19]) Compare Proc. Third Internat. Conference on Bitumious Coal, Vol. II, 797, Pittsburgh 1931.

and compared with the behaviour of paracyanogen and of the nitrogenous carbons prepared from tetraiodoglyoxaline or from tetraiodopyrrole (Pauly and Waltzinger, Ciusa).

3°. The properties of these nitrogenous carbons have been compared to the properties of the nitrogen-carbon-complex in coke from "ash-free" coal.

4°. In nitrogenous carbons of different origin, but of low nitrogen content, the nitrogen-carbon-complex is stable below 800°. In these products the nitrogen is probably present in the form of a surface compound, in which the nitrogen atoms are fixed to surface atoms of the carbon. The nitrogen-carbon-complex in coke is probably of the same nature.

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September 1932.

(Reçu le 7 septembre 1932).